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MONOMERS BY DEGENERATIVE
IODINE TRANSFER

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Enclosed herewith is a certified copy of European Patent Application No. 02078523.4, to support the claim of foreign priority benefits under 35 U.S.C. §119 in connection with the above-identified application.

Respectfully submitted,

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For the President of the European Patent Office

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Si aucun titre n'est indiqué se référer à la description.)

Method for polymerizing ethylenically unsaturated monomers by degenerative iodine transfer

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METHOD FOR POLYMERIZING ETHYLENICALLY UNSATURATED MONOMERS BY DEGENERATIVE IODINE TRANSFER

The invention pertains to a method to prepare a block or gradient co-polymer comprising a step of radically polymerizing a mixture of ethylenically unsaturated monomers.

5 Controlled radical polymerization processes have received much attention over the past decade, because of the possibility to prepare new valuable polymeric materials based on standard conventional monomeric building blocks, such as block or gradient copolymers, and narrow polydispersity functional polymers, with narrower functionality distributions, that can be used in crosslinking
10 compositions.

In the field of "living" radical polymerizations (polymerizations under radical conditions where termination processes of growing radicals are reversible, so that all initiated chains can in principle continue growing as long as monomers
15 and radicals are present), three technologies have been studied in depth:

- *nitroxide mediated polymerizations* (NMP), which are based on homolytic scission of the covalent bond formed between a polymer radical and a nitroxide stable radical;
- *atom transfer radical polymerization* (ATRP), in which a halogen (usually Cl
20 or Br) atom is reversibly transferred between a Cu(I/II) complex and a polymer radical, in a process that encompasses a redox cycle;
- *reversible addition fragmentation chain transfer* (RAFT), which is a process wherein dithioester end groups can be rapidly and reversibly transferred between polymeric radicals.

25 For all these systems, the living character was proven by a typically linear development of molecular weight with conversion, low polydispersities obtained in polymerizations, and the preparation of block copolymers by sequential addition of different monomers.

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Especially ATRP and RAFT have possibilities for numerous applications with respect to the type of monomers used. In ATRP, however, acidic conditions and monomers create problems, whereas the necessary removal of the Cu-amine complexes from the polymers is an expensive and thus unwanted step. In
5 RAFT, these limitations do not occur, but this method suffers in that the polymer chains formed contain dithioester end group, which are strong chromophores. The chromophores can be destroyed by reaction with a nucleophile, which is not always compatible with the functional groups that may be present in the chains, but this is at the expense of an extra reaction step, and leads to low-
10 molecular weight products in the polymer, which may be difficult to remove. Moreover, the dithioester mediating compounds are expensive. NMP has the disadvantage that expensive nitroxides are needed if the process is to be used at acceptably low temperatures for acrylates, whereas methacrylates have intrinsic problems due to the fact that disproportionation as
15 side reaction may occur.

Another type of living radical polymerization process is *degenerative iodine transfer* (DIT) (see for instance, Journal of Physical Organic Chemistry, vol. 8, pp. 306-315 (1995) and Macromolecules, 28, pp. 8051-8056 (1995)). In this
20 case, similarly to the RAFT process, an iodine end group transfers to another polymeric radical, the iodine atom playing a similar role as the dithioester group in RAFT. A chain transfer agent with an iodine atom is used as entry in the DIT process. In general, however, RAFT is considered to be superior to DIT in the rate of end group transfer (more transfer events, lower polydispersity, better
25 control), and its applicability to a broader range of monomers.

DIT was described in Macromolecules, 28, pp. 8051-8056 (1995); Macromolecules, 33(9), p. 3485 (2000); Macromolecules, 32(22), p. 7354 (1999); Macromolecules, 31(9), p. 2809 (1998) for application with styrene
30 monomers, for which it appears to work moderately well (dispersities typically 1.5); for halogenated vinyl monomers like vinyl chloride and fluorinated vinyl species. For acrylates it has been attempted, but results for acrylates showed

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less control (broader polydispersities >2 , indicating a low rate of transfer between acrylate chains) (see: Macromolecules, 28, pp. 8051-8056 (1995)). Processes where acrylates are mentioned in combination with iodine transfer, however, sometimes aim more at obtaining iodine functional chains than on actual living polymerizations (see for instance US 6143848). Block copolymers of acrylates and styrene have been reported in EP 947527, Macromolecules, 28, p. 2093 (1995), and Macromol. Rapid Commun., 2000, 21(13), p. 921.

A few attempts to obtain a degenerative iodine transfer process with methacrylates have been reported, but all of these suggest that methacrylate monomers cannot be used in an acceptable manner in conventional DIT processes using the conventional iodine-functional CTA's (alkyl or perfluoroalkyl iodides), which are applied in the DIT process for e.g. styrene (see for instance Macromolecules, 28, p. 8051 (1995)). High-molecular weight material is formed in the beginning of the polymerization, leading to high polydispersities, without observation of the typical linear development of molecular weight with conversion, which is characteristic for a polymerization with a living character. Another comparison of DIT processes with styrene, acrylate, and methacrylate monomers are disclosed in L. Klumperman at the UNESCO School & South African IUPAC conference on Macromolecular and Materials Science, 29-31 March 1999 and 10-12 April 2000 to be found at <http://www.sun.ac.za/unesco/PolymerED2000/Conf1999/Lectures1999/Klump2.pdf> and www.sun.ac.za/unesco/PolymerED2000/Conf2000/KlumpermanC.pdf. For these reasons DIT is disclosed not to be suitable for polymerizing methacrylates. In US 5439980 this was confirmed in comparative example 2 where it was found that when MMA alone is used with a fluorinated alkyl iodide, only a homopolymer of MMA is produced and a block polymer with an iodide-functional perfluoropolyether is not produced.

Since methacrylates are a very important class of monomers for many applications, with high and low polarity candidates, and various functional side groups available, with high Tg backbones being formed with good chemical

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durability, the inability to use methacrylates is a serious omission in the DIT technology, and a need exists for an effective DIT method allowing the production of polymers based on methacrylates with structures that harvest the advantages of the living nature of the polymerization process.

5

It is therefore an object of the present invention to obtain a DIT process that can be used for polymerizing methacrylate monomers. According to the present invention it was found that the DIT process can be performed in a very favorable way using methacrylates, if the proper start-up process is chosen. We have found that the DIT process can be adapted in a manner of obtaining a high transfer rate of iodine atoms between methacrylate chain ends, leading to better control than DIT of styrenic or acrylate monomers, to low polydispersities closely resembling that of ATRP or RAFT processes, molecular weights increasing with conversion, and the opportunity to prepare well defined block and gradient copolymers.

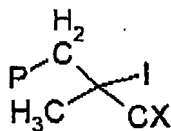
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We have found a novel method wherein iodine-functional methacrylate oligomers are obtained; leading to a DIT process proceeding with a high level of control.

20

To this end the invention pertains to the above method for making a block or gradient co-polymer comprising a step of radically polymerizing a mixture of ethylenically unsaturated monomers in the presence of a) a radical precursor and b) an iodine atom-containing polymer or a mixture of iodine atom-containing polymers, wherein at least 50 mole% has a methacrylate iodide end group,

25



obtainable from a polymerization of ethylenically unsaturated monomers.

The iodide end group has the formula:

wherein P stands for polymer and CX is an acid, ester, amide, or nitrile.

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The iodine atom-containing polymers to be formed initially (forming the "first block" if a block polymer is to be made) should have an end group dominantly of the methacrylate type, i.e. containing more than 50 mole% of iodine-containing methacrylate end groups (methacrylic acid or esters or amides thereof, or methacrylonitrile). Preferably, the molecular weight of this first block is less than 20,000, more preferably less than 10,000. The other co-monomers may be of the (meth)acrylate, styrene, vinyl ester, and maleate type. More preferred is a composition containing more than 70 mole% of iodine-containing methacrylate end groups, most preferred composition have more than 90 mole% of iodine-containing methacrylate end groups.

The polymerization step can be performed with the iodine-containing methacrylate end group polymer (the iodine atom-containing polymer) and a monomer or a mixture of monomers, the composition of which is different from the composition of the iodine-containing methacrylate end group polymer, in the presence of a radical precursor.

Suitable mixtures for making the polymer comprise monomers selected from e.g. acrylic acid, methacrylic acid, methyl acrylate, ethyl acrylate, butyl acrylate, methyl methacrylate, ethyl methacrylate, butyl methacrylate, glycidyl methacrylate, glycidyl acrylate, 2-hydroxyethyl acrylate, 2-ethylhexyl acrylate, potassium methacrylate, cyclohexyl methacrylate, 2-(dimethylamino)ethyl methacrylate, stearyl methacrylate, 2-hydroxyethyl methacrylate, 2-hydroxypropyl methacrylate, vinyl methacrylate, benzyl methacrylate, lauryl methacrylate, diacetone acrylamide, acrylamide, acrolein, methacrylamide, methacrolein, acrylonitrile, methacrylonitrile, styrene, alhamethylstyrene, vinyltoluene, isopropenyl-isopropylideneisocyanatobenzene (mTMI from Cytec), chlorostyrene, butadiene, isoprene, chloroprene, maleic acid, maleimide, methyl maleate, ethyl maleate, propyl maleate, butyl maleate, calcium maleate, allyl maleate, 2-ethylhexyl maleate, octyl maleate, maleic hydrazide, maleic anhydride, fumaric acid, methyl fumarate, ethyl fumarate, propyl fumarate, butyl fumarate, sodium fumarate, fumaronitrile, fumaryl chloride, vinyl acetate, tert-decanoic acid ethenyl ester (VeoVa 10, ex Resolution Performance Products),

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neononanoic acid ethenyl ester (VeoVa 9, ex Resolution Performance Products), vinyl pivalate, and the like. It is not necessary that methacrylate monomers are predominantly present, and this mixture may even be free of methacrylic monomers. If the monomers selected for this polymerization step are predominantly of the methacrylate type, the process can then be repeated to form a third or further block, or gradient copolymers can be obtained, as is obvious for the skilled person.

The weight ratio of the iodine atom-containing polymer to the monomers being polymerized to form the second block, may vary from 1:100 up to 100:1.

10 Preferably, the amounts are selected so that the mole ratio iodine atom-containing polymer : radical precursor is $>0.1n$, more preferably $>0.5n$, wherein n stands for the number of radicals effectively generated per molecule radical precursor (i.e. taking into account the initiator efficiency).

15 The DIT polymerization process of these monomers takes places at temperatures of less than 130°C , preferably less than 110°C , most preferably less than 90°C . It is preferred that mild initiating radicals are used (e.g. C-centered radicals from azo radical initiators). The radical precursors are commonly known in the art, and initiators of the azo-type are most preferred,

20 such as azobisisobutyronitrile (AIBN).

The polymerization process can take place in a batch mode, or in a semi-batch mode, with feeding of several of the reactants to the vessel, or in a process comprising a continuous step. The iodine-functional methacrylate polymers of the DIT type can be transferred and used as a CTA in the subsequent polymerizations process according to the invention.

25 The polymerization can be carried out in bulk, in solvent, in a suspension polymerization process, an emulsion polymerization process, a dispersion polymerization process, or a mini-emulsion polymerization process.

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The iodine atom-containing polymer is made from the monomers as mentioned above, provided that the amount of methacrylic monomers is so selected that at

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least 50 mole% of the end groups are of the methacrylate type. This polymerization is performed in the presence of I_2 or an iodine chain transfer agent (CTA). The term I_2 as used in this application also includes I_2 -precursors (i.e. compounds that can form I_2 *in situ*), such as N-iodosuccinimide, ICl, IBr, and I_3^- .

Iodine chain transfer agents are used in combination with a small amount of radical precursor to obtain a methacrylate polymerization process. When molecular iodine is used, the iodine radical released after one iodine is abstracted by a polymer radical does not reinitiate a methacrylate polymerization, but recombines with another polymer radical. The net effect of molecular iodine is the functionalization of two polymer chains with an iodine end group, in an identical way (J. Polym. Sci. Polym. Lett. Ed. vol. 14, p. 499-502 (1976)). In terms of the polymerization process, it implies that slightly more than 1 equivalent of initiating radicals should be generated, compared to iodine atoms present in the systems as molecular iodine. The mole ratio I_2 : radical precursor is preferably between 0.05n and 0.5n, more preferably between 0.25n and 0.5n, wherein n has the previously given meaning.

Instead of I_2 also an iodine CTA can be used such as a sulfonyliodide, preferably an aromatic sulfonyliodide such as p-toluenesulfonyliodide.

Preferably, the mole ratio sulfonyliodide : radical precursor is $>0.1n$, more preferably $>0.5n$, wherein n stands for the number of radicals effectively generated per molecule radical precursor.

25

It was found to be sometimes advantageous to perform the polymerization in the presence of an epoxide-containing compound. In the presence of epoxide-containing compounds the polydispersity obtained is narrower, leading to coating compositions with a good balance of pot life and curing speed, viscosity and network properties. Such compounds are preferably selected from glycidyl ethers, glycidyl esters, and cycloaliphatic epoxides. Suitably glycidyl-containing monomers are used in the preparation of the iodine atom-containing polymer,

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such as the above mentioned glycidyl methacrylate and glycidyl acrylate. The method according to the invention is preferably performed such that the mole ratio epoxide : iodine atom-containing polymer is > 0.01 , preferable > 0.05 . Similarly, such epoxide-containing compound can also be used in the synthesis of the iodine atom-containing polymer.

Although the essence of the present invention is the radical polymerization of a mixture of ethylenically unsaturated monomers in the presence of a) a radical precursor and b) an iodine atom-containing polymer or a mixture of iodine atom-containing polymers, the invention also pertains to the two-step procedure for making a block or gradient co-polymer comprising a step of radically polymerizing a mixture of ethylenically unsaturated monomers to give iodine atom-containing polymers with at least 50 mole% of iodine methacrylate end group in the presence of a) a radical precursor and b) I_2 or a sulfonyliodide, followed by a step of radically polymerizing a mixture of ethylenically unsaturated monomers in the presence of c) a radical precursor and d) the iodine atom-containing polymer of the first step. The second step may be started before the first step is fully ended. According to this two-step procedure the mole ratio sulfonyliodide : radical precursor is $> 0.1n$, wherein n stands for the number of radicals effectively generated per molecule radical precursor, or wherein the mole ratio I_2 : radical precursor is between $0.05n$ and $0.5n$.

The invention is further illustrated with the following examples.

All reported molecular weights were determined by size exclusion chromatography (RI detection), and expressed in polystyrene equivalent molecular weights, unless specified otherwise. Low-molecular weight materials ($M < 500$), originating e.g. also from initiator in cage recombination products and optionally added low-molecular weight epoxides, were not taken into account for this determination of the main polymer envelope in the molecular mass distribution. The following abbreviations are used: MMA = methyl methacrylate, GMA = glycidyl methacrylate; BA = butylacrylate, BMM = butyl methacrylate,

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HEMA = hydroxyethyl methacrylate, HMMA = hydroxymethyl methacrylate,
SEC = size exclusion chromatography.

The effect of copolymerizing methacrylates and acrylates on the molar mass distribution, as a measure for the extent of control, is illustrated by the following
5 examples. It can be seen that the amount of control is lost if the fraction of acrylate monomers becomes too high. These experiments show that upon using MMA/BA ratios with a good control gradient, copolymers are obtained due to the higher polymerization reactivity of MMA vs. BA.

10 Example 1

A reaction vessel was charged with 21.25 g of MMA, 5.32 g of BA, 20 g of butyl acetate, 1.54 g of I₂, and 2.258 g of 2,2'-azobis(2,4-dimethylvaleronitrile), degassed and maintained under a nitrogen atmosphere. The temperature was raised to 67°C, and the reaction was continued for 8 h. After 1 h and 40 min, the
15 brown iodine color was observed to fade, an observation that coincides with a steep increase of conversion with time, after the inhibition period in the presence of molecular iodine. SEC analysis of a sample taken after this period (conversion 88%) yields an Mn of 2325, and an Mw/Mn of 1.31, Mz/Mw 1.25.

20 Example 2

A reaction vessel was charged with 15.96 g of MMA, 10.66 g of BA, 20 g of butyl acetate, 1.53 g of I₂, and 2.26 g of 2,2'-azobis(2,4-dimethylvaleronitrile), degassed and maintained under a nitrogen atmosphere. The temperature was raised to 64°C, and the reaction was continued for 8 h. After 2 h the brown
25 iodine color was observed to fade, an observation which coincides with a steep increase of conversion with time, after the inhibitive period in the presence of molecular iodine. SEC analysis of a sample taken after this period (conversion 82%) yields an Mn of 2210, and an Mw/Mn of 1.48, Mz/Mw 1.47.

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Example 3

A reaction vessel was charged with 10.62 g of MMA, 15.96 g of BA, 20 g of butyl acetate, 1.53 g of I₂, and 2.267 g of 2,2'-azobis(2,4-dimethylvaleronitrile), degassed and maintained under a nitrogen atmosphere. The temperature was raised to 64°C, and the reaction was continued for 20 h. After 2 h, the brown iodine color was observed to fade. SEC analysis of a sample taken after this period (conversion 95%) yields an Mn of 2430, an Mw/Mn of 2.04, and an Mz/Mw of 2.16.

10 Comparison Example 4

A reaction vessel was charged with 5.31 g of MMA, 21.26 g of BA, 20 g of butyl acetate, 1.52 g of I₂, and 2.267 g of 2,2'-azobis(2,4-dimethylvaleronitrile), degassed and maintained under a nitrogen atmosphere. The temperature was raised to 64°C, and the reaction was continued for 20 h. SEC analysis of a sample taken after this period (conversion 95%) yields an Mn of 2580, an Mw/Mn of 2.17, and an Mz/Mw of 2.23.

Comparison Example 5

A reaction vessel was charged with 26 g of BA, 20 g of butyl acetate, 1.67 g of I₂, and 2.267 g of 2,2'-azobis(2,4-dimethylvaleronitrile), degassed and maintained under a nitrogen atmosphere. The temperature was raised to 64°C, and the reaction was continued for 4 h. SEC analysis of a sample taken after this period (conversion 93%) yields an Mn of 2300, an Mw/Mn of 1.92, and an Mz/Mw of 2.07.

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Example 6

A reaction vessel was charged with 11.01 g of MMA, 11.00 g of BA, 8.06 g of HMMA, 20 g of butyl acetate, 1.523 g of I₂, and 2.26 g of 2,2'-azobis(2,4-dimethylvaleronitrile), degassed and maintained under a nitrogen atmosphere. The temperature was raised to 64°C, and the reaction was continued for 7 h. SEC analysis of a sample taken after this period (conversion 98%) yields an Mn

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4800, an Mw/Mn of 1.26, and an Mz/Mw of 1.31. Monomers with functional side groups may also be used

Example 7

- 5 To a reaction vessel, maintained at 65°C, over a period of 2 h, a solution was fed consisting of 36.49 g of BMA, 6.57 g of GMA, 3.69 g of I₂, and 5.42 g of 2,2'-azobis(2,4-dimethylvaleronitrile) and 16 g of Dowanol PM (solvent) to obtain a first BMA-co-GMA block of Mn 2880, Mn/Mw 1.25, Mz/Mw 1.19.

10 Example 8

- A reaction vessel was charged with 11.02 g of MMA, 11.01 g of BA, 20.06 g of butyl acetate, 1.52 g of I₂, and 2.26 g of 2,2'-azobis(2,4-dimethylvaleronitrile), degassed and maintained under a nitrogen atmosphere. The temperature was raised to 64°C, and the reaction was monitored until the dark iodine color starts to fade (conversion 9%). At this point, 5.29 g of methacrylic acid and 2.75g of Cardura E-10 epoxide were added in one shot and the reaction was continued for 4 h. SEC analysis of a sample taken after this period (conversion 99%) yields an Mn 2928, an Mw/Mn of 1.32, and an Mz/Mw of 1.28.

20 Example 9

- To the polymer of Example 7, a mixture of 27.9 g of HEMA and 0.469 g of 2,2'-azobis(2,4-dimethylvaleronitrile) was added, together with 10 ml of Dowanol PM, at a temperature of 64°C. After 4 h, a block copolymer was obtained with Mn 2430, Mw/Mn 1.46, Mz/Mw 1.31.

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Example 10

- A reaction vessel was charged with 30 g of MMA, 20 g of butyl acetate, 1.516 g of I₂, and 2.259 g of 2,2'-azobis(2,4-dimethylvaleronitrile), degassed and maintained under a nitrogen atmosphere. The temperature was raised to 66°C, and the reaction was continued for 4.5 h. At this point, the conversion was 81%, an Mw of 3000 (Mz/Mw 1.26), and a mixture of 5.01 g of HEMA, 5.08 g of BMA, 6 g of butyl acetate and 0.0097 g of 2,2'-azobis(2,4-dimethylvaleronitrile) was

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added, and the reaction was continued for another 3.5 h. The final block copolymer had an Mw of 3580, Mz/Mw 1.33).

Example 11

- 5 A reaction vessel was charged with 30.05 g of MMA, 20.05 g of butyl acetate, 1.52 g of I₂, 2.26 g of 2,2'-azobis(2,4-dimethylvaleronitrile), degassed and maintained under a nitrogen atmosphere. The temperature was raised to 65°C, and the reaction was continued for 6.5 h. SEC analysis of a sample taken after this period (conversion 97%) yields an Mn of 2881, an Mw/Mn of 1.14, Mz/Mw
- 10 1.12.

Three days later, to this block was slowly added a mixture of 60 g of BMA, 35.0 g of butylacetate, and 0.80 g of 2,2'-azobis(2,4-dimethylvaleronitrile) over a period of 3.5 h at 65°C, and polymerized for an additional 2 h to obtain a block copolymer with Mn 7200, Mw/Mn 1.67, Mz/Mw 1.47.

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Example 12

- A reaction vessel was charged with 30.0 g of MMA, 20 g of butyl acetate, 2.54 g of I₂, 3.83 g of 2,2'-azobis(2,4-dimethylvaleronitrile), and 2.33 g of Cardura E-10 (versatic acid glycidyl ester), degassed and maintained under a nitrogen
- 20 atmosphere. The temperature was raised to 64°C, and the reaction was continued for 5 h. SEC analysis of a sample taken after this period (conversion 95%) yields an Mn of 2990, an Mw/Mn of 1.20, Mz/Mw 1.16.

Example 13

- 25 To the polymer of Example 12 was added a mixture of 2.57 g of BMA, 2.5 g of butyl acetate, and 0.257 g of 2,2'-azobis(2,4-dimethylvaleronitrile). The reaction was continued for an additional 2 h (conversion 99%), to yield a block copolymer Mn 3263, Mw/Mn 1.21, Mz/Mw 1.18.

Example 14

A reaction vessel was charged with 30.05 g of MMA, 20.03 g of butyl acetate, 2.54 g of I₂, 3.79 g of 2,2'-azobis(2,4-dimethylvaleronitrile), degassed and

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maintained under a nitrogen atmosphere. The temperature was raised to 64°C, and the reaction was continued for 7 h. SEC analysis of a sample taken after this period (conversion 97%) yields an Mn of 1710, an Mw/Mn of 1.16, Mz/Mw 1.14.

- 5 To this block was added a mixture of 15.04 g of BMA, 10.06 g of butyl acetate, and 0.27 g of 2,2'-azobis(2,4-dimethylvaleronitrile) with a feeding rate of 0.187 ml/min. The polymerization of the second block was continued for a total time of 4.5 h to yield a block copolymer Mn 2390, Mw/Mn 1.31, Mz/Mw 1.38.
- 10 Next to the I₂ route, a good start of a DIT process with methacrylates can also be made if an iodine CTA, such as tosyl iodide, is used with a high chain transfer coefficient for methacrylates (CTC>1).

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CLAIMS

1. A method for making a block or gradient co-polymer comprising a step of radically polymerizing a mixture of ethylenically unsaturated monomers in the presence of a) a radical precursor and b) an iodine atom-containing polymer or a mixture of iodine atom-containing polymers, wherein at least 50 mole% has a methacrylate iodide end group, obtainable from a polymerization of ethylenically unsaturated monomers.
2. The method according to claim 1 wherein the mole ratio iodine atom-containing polymer : radical precursor is $> 0.1n$, wherein n stands for the number of radicals effectively generated per molecule radical precursor.
3. The method according to claim 1 or 2 wherein the temperature during the polymerization steps is lower than 130°C , preferably lower than 110°C , and most preferably lower than 90°C .
4. The method according to any one of claims 1-3 wherein the polymerization is performed in the presence of an epoxide-containing compound.
5. The method according to claim 4 wherein the mole ratio epoxide : iodine atom-containing polymer is > 0.01 , preferably > 0.05 .
6. A method according to any one of claims 1-5 wherein the iodine atom-containing polymer is obtainable by polymerization of a mixture of ethylenically unsaturated monomers, comprising at least 50 mole% of methacrylate moiety-containing monomers in the presence of a) a radical precursor and b) iodine or an iodine atom-containing chain transfer agent.

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- 5 7. A method for making a block or gradient co-polymer comprising a step of radically polymerizing a mixture of ethylenically unsaturated monomers to an iodine atom-containing polymer, wherein at least 50 mole% has a methacrylate iodide end group, in the presence of a) a radical precursor and b) I_2 , followed by a step of radically polymerizing a mixture of ethylenically unsaturated monomers in the presence of c) a radical precursor and d) the iodine atom-containing polymer of the first step.
- 10 8. A method for making a block or gradient co-polymer comprising a step of radically polymerizing a mixture of ethylenically unsaturated monomers to an iodine atom-containing polymer, wherein at least 50 mole% has a methacrylate iodide end group, in the presence of a) a radical precursor and b) a sulfonyliodide, followed by a step of radically polymerizing a mixture of ethylenically unsaturated monomers in the presence of c) a radical precursor and d) the iodine atom-containing polymer of the first step.
- 15 9. The method of claim 7 wherein the mole ratio wherein the mole ratio I_2 : radical precursor is between $0.05n$ and $0.5n$, wherein n stands for the number of radicals effectively generated per molecule radical precursor.
- 20 10. The method of claim 8 wherein the mole ratio sulfonyliodide : radical precursor is $> 0.1n$, wherein n stands for the number of radicals effectively generated per molecule radical precursor.

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ABSTRACT

5 The invention pertains to a method for making a block or gradient co-polymer comprising a step of radically polymerizing a mixture of ethylenically unsaturated monomers in the presence of a) a radical precursor and b) an iodine atom-containing polymer or a mixture of iodine atom-containing polymers, wherein at least 50 mole% has a methacrylate iodide end group, obtainable from a polymerization of ethylenically unsaturated monomers.